

Molecular and dissociative adsorption of multiple hydrogens on transition metal decorated C_{60}

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Recently we have predicted [Phys. Rev. Lett.**94**, 175501 (2005)] that Ti-decorated carbon nanotubes can adsorb up to 8-wt% hydrogen at ambient conditions. Here we show that a similar phenomenon occurs in light transition-metal decorated C_{60} . While Sc and Ti prefer the hexagon (H) sites with a binding energy of 2.1 eV, V and Cr prefer double-bond (D) sites with binding energies of 1.3 and 0.8 eV, respectively. Heavier metals such as Mn, Fe, and Co do not bond on C_{60} . Once the metals are adsorbed on C_{60} , each can bind up to four hydrogen molecules with an average binding energy of 0.3-0.5 eV/H₂. At high metal coverage, we show that a C_{60} can accommodate six D-site and eight H-site metals, which can reversibly adsorb up to 56 H₂ molecules, corresponding to 7.5 wt%.

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An efficient storage media for hydrogen is crucial for the advancement of hydrogen and fuel-cell technologies.¹ Currently, a lot of effort is being devoted to engineering nanomaterials so that they dissociate H₂ molecules into H atoms and reversibly adsorb hydrogen molecules at ambient conditions.¹⁻¹⁰ Much work has focused on carbon-based materials such as nanotubes,²⁻¹² and metal hydrides such as alanates.¹³ It is found that, while the hydrogen-carbon interaction is too weak for hydrogen storage at ambient conditions,¹¹ the metal-hydrogen interaction is too strong. Very recently we have shown¹⁴ a novel way to overcome this difficulty by forming artificial metal-carbide-like structures on single-wall carbon nanotubes (SWNT). From accurate first-principles calculations, we show that a single Ti atom adsorbed on a SWNT can strongly bind up to four hydrogen molecules.¹⁴ At large Ti coverage we find that a (8,0) SWNT can store hydrogen molecules up to 8-wt%, exceeding the minimum requirement of 6-wt% for practical applications. These results can be explained by a simple Dewar-Chatt-Duncanson model,^{15,16} where the interaction is caused by donation of charge from the highest occupied orbital of the ligand to the metal empty states and a subsequent back donation from the filled *d* orbitals to the lowest unoccupied orbital of the ligand.

Here we show that a similar phenomenon occurs in light transition-metal decorated C_{60} molecules. We first discuss several possible adsorption sites for a single Ti atom on a C_{60} molecule. Then we show how a single Ti atom on a C_{60} can bind up to four hydrogen molecules via Kubas interaction.^{15,16} Multiple metal coverage cases, yielding up to 8-wt% hydrogen storage, are discussed next. Finally, we briefly describe the results for other transition metals from Sc to Co.

The energy calculations were performed within a plane-wave implementation¹⁷ of the Generalized Gradient Approximation¹⁸ to Density Functional Theory. We used Vanderbilt ultrasoft pseudopotentials¹⁹ treating the

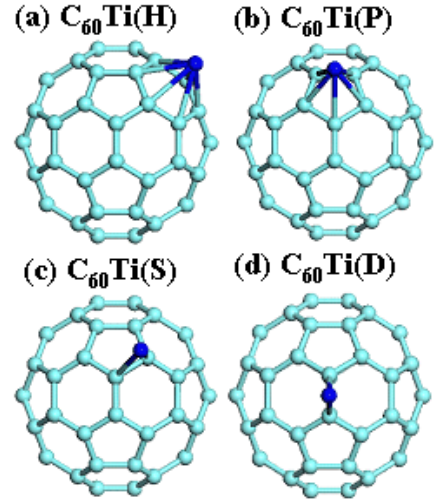


FIG. 1: A single Ti atom adsorbed at hexagonal (H) (a) and pentagonal (P) (b) hollow sites, and single (S) (c) and double (D) (d) bond sites of a C_{60} molecule, respectively.

following electronic states as valence: Ti 3*s*, 3*p*, 3*d*, and 4*s*, C 2*s* and 2*p*, and H 1*s*. A cutoff energy of 350 eV was found to yield total energies converged to within 0.5 meV/atom. We used a cubic supercell of $a = 16$ Å for single-metal C_{60} systems and $a = 20$ Å for full-coverage cases. We also made spin-polarized calculations for cases where the ground state of the metal-coated C_{60} is magnetic. Conjugate-gradient structural relaxations were considered to be converged when forces on atoms were smaller than 0.2 eV/Å.

Figure 1 shows the four possible adsorption sites on a C_{60} molecule that are considered in this study. The C_{60} molecule has the truncated-icosahedral symmetry with twenty hexagons (H), twelve pentagons (P), thirty C-C double bonds (D) between two hexagons, and sixty

TABLE I: Calculated Ti-C and C-C bond distances, Mulliken charges, spins, and binding energies for a single Ti atom adsorbed at the four different sites of a C_{60} molecule shown in Fig. 1. For bare C_{60} the calculated double and single bond lengths are 1.44 and 1.38 Å, respectively.

	$C_{60}Ti(H)$	$C_{60}Ti(P)$	$C_{60}Ti(D)$	$C_{60}Ti(S)$
$d(Ti-C)$ (Å)	2.27	2.33	2.10	2.24
$d(C-C)$ (Å)	1.42/1.45	1.44	1.52	1.48
$Q(Ti)$ (e)	1.39	1.09	0.99	0.84
$S(Ti)$	$0.99 \hbar$	$1.40 \hbar$	$1.13 \hbar$	$1.54 \hbar$
$E_B(Ti)$ (eV)	2.098	1.633	1.837	1.220

C-C single bonds (S) which are between pentagon and hexagon carbon rings. We calculated the binding energy of a single Ti atom at these sites. The results are given in Table I along with relevant structural parameters. The binding energy is defined as

$$E_B(Ti) = E(C_{60}) + E_{\text{spol}}(Ti) - E_{\text{spol}}(C_{60}Ti), \quad (1)$$

where the E_{spol} energies are obtained from spin-polarized calculations. Hence, a positive binding energy indicates the system is stable.

Our results indicate that the H-site is the most stable configuration for $C_{60}Ti$, with a binding energy of 2.1 eV. The D-site comes next with the shortest Ti-C bonds among the four possible configurations. In all cases, we have a charge transfer of about one electron to the C_{60} molecule. The S-site is the least stable adsorption site and therefore we do not consider it any further.

Figure 2(a) shows the energy variation, obtained from spin-unpolarized calculations, as a single H_2 molecule approaches $C_{60}Ti(D)$. The energy first decreases slowly as the hydrogen approaches the $C_{60}Ti(D)$ complex. However, as the charge overlap gets large, the H_2 molecule is attracted towards the Ti atom with a sharp decrease in energy. At this point, the H_2 molecule is still intact with a significantly increased H-H bond length of 0.9 Å. The second pronounced decrease in energy is associated with the dissociation of the H_2 molecule into two H atoms. At this point, the H-H distance increases up to 2.94 Å. The interaction between H_2 and $C_{60}Ti(D)$ is always attractive and therefore H_2 is adsorbed onto the Ti atom without having to overcome any energy barrier. The final geometry is shown in the inset to Fig. 2(a).²⁰ In order to calculate the binding energy for this dissociative adsorption, we computed the total energies of the $C_{60}Ti(D)$ and H_2 reactants and the $C_{60}Ti(D)H_2$ final product (dashed lines in Fig. 1(a)) from spin-polarized calculations. We obtained a binding energy of 1.16 eV (Fig. 2(a)).

Figure 2(b) shows the energy variation as two H_2 molecules approach the TiH_2 group, one from each side. As in the single-adsorption case, the energy always decreases, slowly at the beginning and very rapidly at the later stage when the two hydrogen molecules become strongly attached to the $C_{60}Ti(D)H_2$ complex. We denote the final product by $C_{60}Ti(D)H_2-2H_2$. In the final

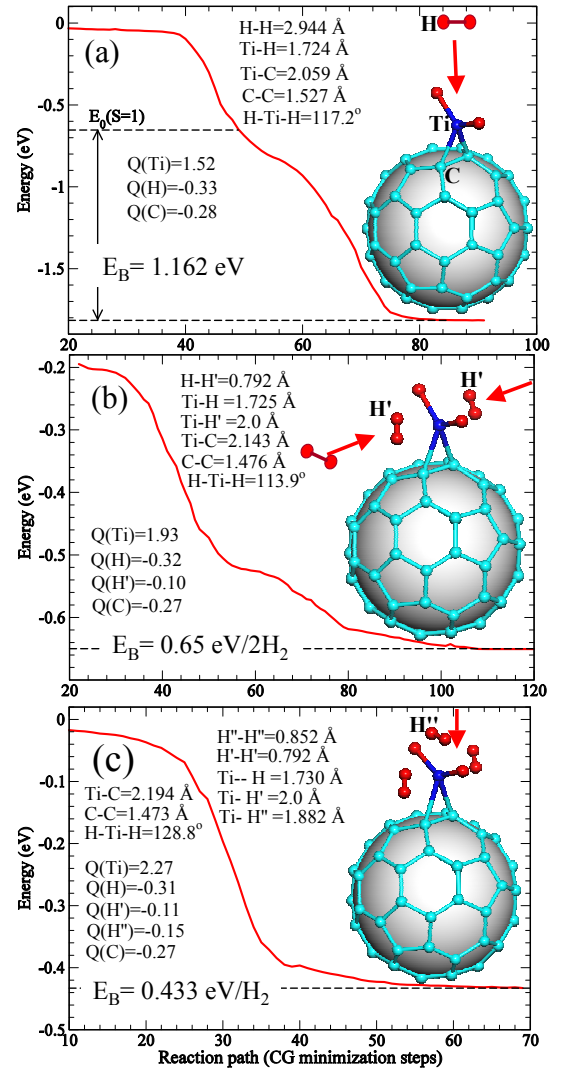


FIG. 2: Energy along the reaction paths for dissociative and molecular adsorption of H_2 over a single $C_{60}Ti(D)$. (a) $H_2 + C_{60}Ti(D) \rightarrow C_{60}Ti(D)H_2$. (b) $2H_2 + C_{60}Ti(D)H_2 \rightarrow C_{60}Ti(D)H_2-2H_2$. (c) $H_2 + C_{60}Ti(D)H_2-2H_2 \rightarrow C_{60}Ti(D)H_2-3H_2$. In all the cases, the relevant structural parameters are given. The zero of energy is taken as the sum of the energies of two reactants.

configuration the two H_2 molecules were rotated by 90° , as shown in Fig. 2(b). The total energy change upon adsorption is about 0.65 eV (i.e. 0.325 eV/ H_2). Unlike in the first adsorption, the second and third H_2 molecules do not dissociate, but display a rather elongated bond of 0.79 Å.

Figure 2(c) shows the energy evolution when a fourth hydrogen molecule approaches the $C_{60}Ti(D)H_2-2H_2$ system from the top. The energy again decreases continuously, indicating a zero-energy barrier. The final product, denoted by $C_{60}Ti(D)H_2-3H_2$, is shown in the inset. The fourth adsorption results in an energy gain of 0.433 eV/ H_2 . The H-H distance of the top H_2 is 0.85 Å. Several attempts to add a fifth hydrogen molecule at a

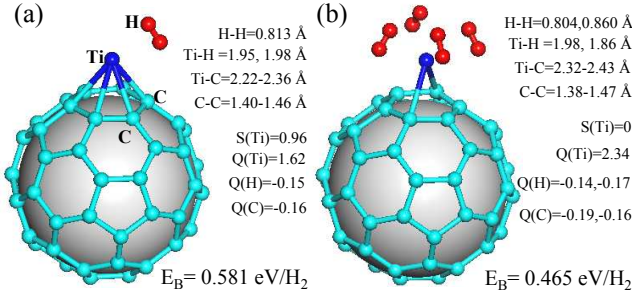


FIG. 3: Molecular adsorption of a single (a) and four H₂ (b) on C₆₀Ti(H). The binding energies and relevant structural parameters are given.

variety of positions failed, suggesting a limit of four H₂ per Ti. However, in view of a recent study²¹ showing that it is possible to attach twelve H atoms to a single transition metal, there might well be other transition paths that could yield more than four hydrogen molecules per C₆₀Ti.

Next we discuss the adsorption properties of a Ti at the H-site of the C₆₀, as shown in Fig. 3. For the first H₂ adsorption, we find that the molecule does not dissociate, unlike in the case of Ti at a D-site (Fig. 2(a)). The reason is that the Ti atom is adsorbed very strongly at the H-site and, therefore, there is not enough charge left in the Ti to transfer to the σ^* orbital of the hydrogen molecule and thus break it.¹⁴ The binding energy is about 0.58 eV and the H-H bond length 0.813 Å. Additional H₂ molecules can be adsorbed, without any activation-energy barrier, up to four H₂ per Ti. The resulting system, which is shown in Fig. 3(b), is denoted by C₆₀Ti(H)-4H₂. The final configuration is very symmetric, and all the hydrogen molecules benefit equally from the bonding with the Ti atom. The average binding energy per H₂ is about 0.465 eV, i.e. slightly smaller than that obtained for the first adsorption. We have also calculated the binding energy for the isomer C₆₀Ti(H)H₂-3H₂, where the first H₂ is bonded to Ti dissociatively. We find that this isomer is about 0.1 eV higher in energy than C₆₀Ti(H)-4H₂.

The results for the adsorption of hydrogens at the P-site Ti are summarized in Fig. 4. The first adsorption is found to be dissociative without activation energy. The binding energy is about 0.615 eV, i.e. significantly smaller than that for Ti at the D-site (Fig. 2(a)), but the adsorption is still dissociative unlike for Ti at the H-site (Fig. 3(a)). The two isomers, C₆₀Ti(P)H₂-3H₂ (Fig. 4(b)) and C₆₀Ti(P)-4H₂ (Fig. 4(c)), are found to be almost degenerate and yield a binding energy of 0.43 eV/H₂.

Up to this point, we have discussed the interaction of H₂ with a single Ti atom bonded to a C₆₀, but clearly one can imagine attaching additional Ti atoms to a C₆₀, thereby increasing the hydrogen-storage capacity. In order to show the feasibility of this approach, we consider several cases. Figure 4(d) shows the full-coverage case where all the P-sites of a C₆₀ molecule host a Ti atom, each of which binds four H₂ molecules. The calculated

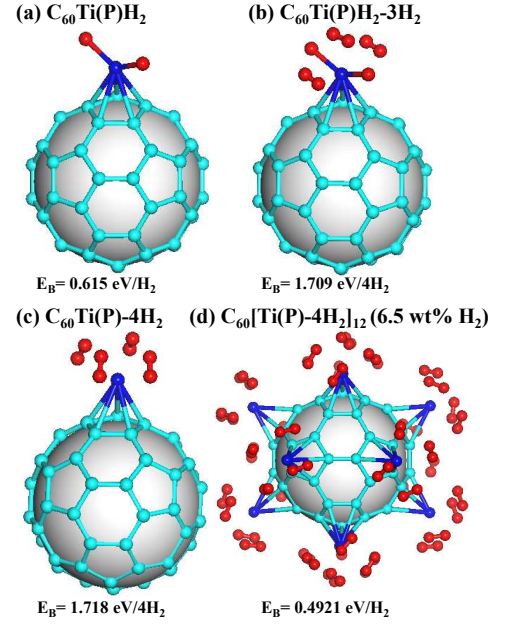


FIG. 4: Optimized structures of C₆₀ with various coverages of Ti(P) and H₂. (a) One H₂ molecule adsorbed on a single Ti(P). (b-c) Two isomers with four H₂ molecules adsorbed on a single Ti(P). (d) Full coverage case with twelve Ti(P)H₂ groups.

binding energy is 0.492 eV/H₂, which is slightly higher than that of the single-coverage case of Fig. 4(c). A possible reason for this is that the C₆₀ distorts more in the single-coverage case than in the full-coverage one, which is more symmetric. In fact, we see the same effect in the binding energy of Ti atom at the P-site: we get 1.633 eV (see Table I) for a single Ti atom and 2.115 eV/Ti when there are Ti atoms at every P-site. These results are quite promising, as they suggest that it should be possible to synthesize the fully-covered systems. We note that early experiments have already indicated that it may be possible to coat C₆₀²² and SWNT²³ by light-transition metals.

Figure 5(a) shows the case in which six Ti atoms are adsorbed at D-sites (i.e. sites on two-fold axes of the C₆₀ molecule). As in the case of full Ti(P) coverage, the binding energy per H₂ (0.592 eV) is slightly larger than that of the single-Ti case (0.559 eV). Interestingly, one can further add eight more Ti atoms at the hexagonal faces (i.e. those along the [111] directions), yielding a total of 14 Ti atoms per C₆₀. The fully hydrogenated case for this Ti coverage is shown in Fig. 5(b). The average binding energy is 0.522 eV/H₂, in remarkable agreement with the 0.505 eV/H₂ based on the energies for single coverage case. This indicates that the 14 Ti atoms and 56 hydrogen molecules shown in Fig. 4(b) are not too close to each other, which in turn suggests that the system is able to host many titaniums and hydrogens. In fact, the configuration shown in Fig. 5(b), which has the chemical formula C₆₀Ti₁₄H₅₆, stores approximately 7.5-wt%

TABLE II: Calculated TM-C and C-C bond distances, Mulliken charges, spins and binding energies for a single TM atom (TM = Sc, Ti, V, etc.) adsorbed on a C_{60} molecule.

Properties	$C_{60}Sc(H)$	$C_{60}Ti(H)$	$C_{60}V(D)$	$C_{60}Cr(D)$	$C_{60}Mn(D)$	$C_{60}Fe(D)$	$C_{60}Co(D)$
$d(TM-C)$ (Å)	2.29	2.27	2.18	2.09	2.30	2.28	2.26
$d(C-C)$ (Å)	1.42/1.46	1.42/1.45	1.46	1.50	1.45	1.45	1.45
$Q(TM)$ (e)	1.55	1.39	0.78	0.91	0.97	0.86	0.76
$S(TM)$	0.24 \hbar	0.99 \hbar	2.0 \hbar	2.35 \hbar	2.99 \hbar	2.53 \hbar	1.54 \hbar
$E_B(TM)$ (eV)	2.127	2.098	1.308	0.760	-0.017	-0.130	-0.503
$E_B(H_2)$ (eV)	0.300	0.454	0.497	0.239	-0.092	-	-

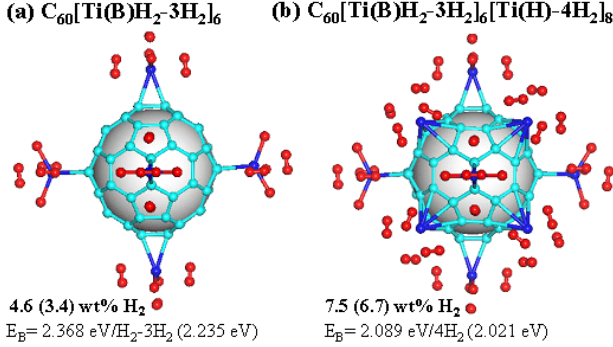


FIG. 5: Two Ti-coated C_{60} systems with high-density H-coverage. They correspond to 4.3-wt% and 7.5-wt% H-storage if all hydrogens can be released, and to 3.4-wt% and 6.7-wt% H-storage if only molecularly adsorbed hydrogens can be released.

hydrogen.

It is important to know if the results reported above for the $C_{60}Ti$ system hold for other transition metals. Therefore we have also studied the transition metals from Sc to Co. Table II summarizes our results for the binding energies and relevant structural parameters. We find that while Sc and Ti prefer the H-site, V and Cr prefer the D-site. The binding energies monotonically decrease as we move from left to right of the periodic table. In fact, for Mn, Fe, and Co we obtained negative binding energies,

indicating that the $C_{60}TM$ complex is not stable. We also found that the other transition metals are able to adsorb hydrogen in a way that is similar to that discussed above for Ti. The last line in Table II indicates the average binding energy per H_2 in $C_{60}TMH_2-3H_2$ configurations. It increases from 0.3 eV/ H_2 for Sc to 0.5 eV/ H_2 for V. Then, it decreases to 0.24 eV/ H_2 for Cr, and finally the complex becomes unstable for heavier transition metals.

In conclusion, we have used state-of-the-art first-principles calculations to show that light transition-metal decorated C_{60} molecules exhibit remarkable hydrogen storage properties. Metals bonded on the D-site dissociate the first H_2 molecule without any activation-energy barrier, and then reversibly bond three more hydrogen molecules. However, metals adsorbed at the H-sites bind four hydrogen molecules without dissociating any of them. Combining these two binding sites, we show that a single C_{60} is able to bind up to 56 H_2 molecules, corresponding to 7.5-wt% H-storage capacity. These results, along with our previous work on Ti-decorated SWNT,¹⁴ suggest a new direction towards high-capacity hydrogen storage materials by decorating nanostructured systems with light transition-metals. The transition-metal-hydrogen bond is explained by the Dewar-Chatt-Duncanson model,^{15,16} and has the right strength for room temperature reversible hydrogen storage.

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